REACTION OF PHENOXAZINE AND PHENOTHIAZINE WITH TETRACYANOQUINODIMETHANE*

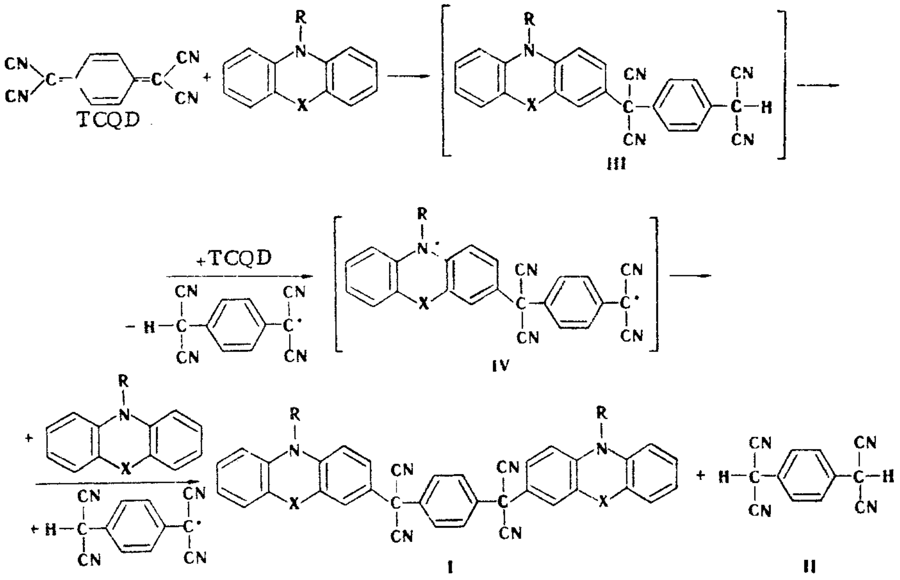
B. P. Bespalov and E. V. Getmanova

UDC 547.867.6

The corresponding α,α'-di(3-phenoxazinyl)-p-phenylenedimalononitriles and p-phenylenedimalononitrile are formed in the reaction of tetracyanoquinodimethane with phenoxazine and its heterocyclic analogs. The reaction scheme is discussed.

It was previously found that tetracyanoquinodimethane (TCQD) reacts readily with pyrroles and indoles to give 1,6-addition products [2]. Heterocyclic nitrogen compounds that have weaker donor properties such as pyridines and pyrazoles do not react with TCQD.

We have shown that TCQD reacts with phenoxazines and phenothiazines to give a new type of adduct, viz., the product of addition of two molecules of the donor to the TCQD (I) molecule, and p-phenylenedimalononitrile (II). In addition, a small amount of a colorless substance that turned blue under the influence of UV light, which is similar with respect to its behavior to the usual products of 1,6-addition to the quinoid system of TCQD and has structure III, was detected in the reaction mixture by thin-layer chromatography (TLC).



X = O, S; R = H, CH_3

We assume that the reaction takes place in two steps. An intermediate 1,6-addition product (III) is formed in the first step. The fact of the formation of a mixed 1,6-addition product (VI) in addition to I when the product (V) of 1,6 addition of N,N-dimethylaniline to TCQD is refluxed in alcohol in the presence of TCQD and phenoxazine or phenothiazine serves as evidence for this. The formation of VI is not observed when this reaction is carried out without TCQD.

---

*Communication 7 from the series "The chemistry of quinomethanes." See [1] for Communication 6.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 317-320, March, 1981. Original article submitted May 29, 1980.

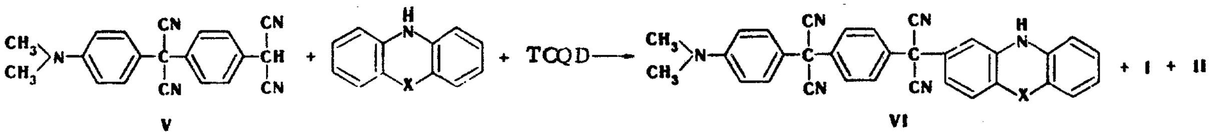
0009-3122/81/1703- 0225$07.50 © 1981 Plenum Publishing Corporation

TABLE 1. Constants, Yields, and Results of Analysis of α-R-α'-R¹-p-Phenylenedimalononitriles (Ia-c, VIa,b)

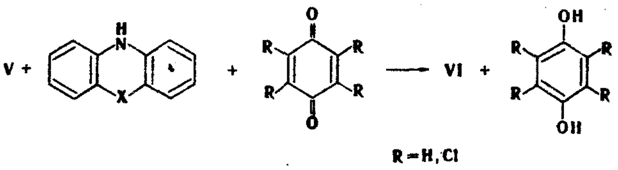
Compound	R	R'	mp, °C	λmax, nm colored form (CH_3OH)	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
Ia	Phenoxazinyl	Phenoxazinyl	296—297*	497	76,2	3,9	14,6	$C_{36}H_{20}N_6O_2$	76,2	3,6	14,8	60
Ib	Phenothiazinyl	Phenothiazinyl	280—281†	542	71,9	3,9	14,0	$C_{36}H_{20}N_6S_2$	72,0	3,4	14,0	34
Ic	N-Methylphenothiazinyl	N-Methylphenothiazinyl	200⁶ (dec.)*	539	72,1	4,0	12,7	$C_{38}H_{24}N_6S_2$	72,6	3,8	13,4	41
VIa	Phenoxazinyl	N,N-Dimethylaminophenyl	245—247	495	75,6	4,8	16,1	$C_{32}H_{22}N_6O$	75,9	4,4	16,6	52
VIb	N,N-Dimethylaminophenyl	N,N-Dimethylaminophenyl	272†	538	73,6	4,0	15,8	$C_{32}H_{22}N_6S$	73,6	4,2	16,1	62

---

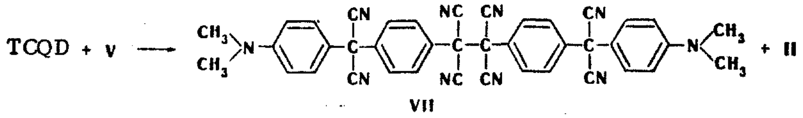
*From acetone.
†Form acetonitrile.



The second step in the reaction of TCQD with phenoxazines and phenothiazines is probably oxidation of addition product III by the acceptor to give radical IV, which then reacts with phenoxazine or phenothiazine to give I. Chloranil or benzoquinone can be used in place of TCQD as the oxidizing agent.



The existence of intermediate radical IV is confirmed by the isolation of coupling product VII, if TCQD or chloranil is refluxed in acetonitrile with V.

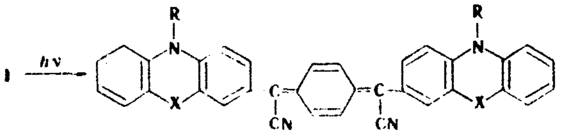


To establish the structure of I we studied the reaction of TCQD with N-methylphenothiazine, which proceeds in the same way as its reaction with phenothiazine. This excludes reaction at the nitrogen atom in the phenothiazine molecule in the first step. If the para position relative to the nitrogen atom in the phenothiazine molecule is occupied, as, for example, in 3,7-dimethylphenothiazine, the reaction with TCQD stops at the step involving the formation of the molecular complex even under severe conditions (refluxing in dimethylformamide). Thus the addition of TCQD in the first step takes place in the para position relative to the nitrogen atom in the donor molecule.

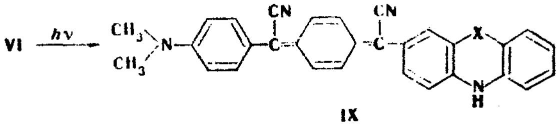
To ascertain the site of incorporation of radical IV in the phenothiazine molecule in the second step we carried out the reaction of TCQD and V with 3,7-dimethylphenothiazine. The formation of an addition product of the VI type is not observed in this case. Thus in the second step the addition of radical IV also takes place in the para position relative to the nitrogen atom in the donor molecule.

Compounds I and VI are crystalline colorless substances; their constants are presented in Table 1.

Under the influence of UV light, I and VI are converted to deeply colored red to violet substances. In analogy with the formation of dyes from p-phenylenedimalononitrile derivatives, we assigned structures VIII and IX, respectively, to them.



VIII



IX

Compounds VIII and IX are unstable and gradually decompose upon irradiation; we were therefore unable to isolate and characterize them in pure form. The λ_{max} values of the colored forms obtained when the light-sensitive compounds are irradiated are presented in Table 1.

EXPERIMENTAL

The TCQD was purified by recrystallization from acetone with activated charcoal. The phenoxazine, phenothiazine, and N-methylphenothiazine were purified by recrystallization from benzene with activated charcoal. The UV spectra were recorded with a Hitachi MSP-50 spectrophotometer.

The 3,7-dimethylphenothiazine was obtained in 51% yield from p-ditolylamine and sulfur as in the preparation of phenothiazine by the method in [3] and had mp 238°C.

The α-[4-(N,N-dimethylamino)phenyl]-p-phenylenedimalononitrole (V) was obtained by the method in [4].

α,α'-Di(3-phenoxazinyl)-p-phenylenedimalononitrile (Ia). A mixture of 1 mmole of TCQD and 1 mmole of phenoxazine was refluxed in 50 ml of alcohol for 10 h, and the resulting precipitate was removed by filtration, dried, and recrystallized twice with activated charcoal to give Ia. The mother liquor was evaporated to dryness, the residue was refluxed in 15 ml of benzene, and the insoluble residue was removed by filtration and recrystallized from acetone to give p-phenylenedimalononitrile (10%) with mp 244-245°C.

α,α'-Di(3-phenothiazinyl)-p-phenylenedimalononitrile (Ib). A mixture of 1 mmole of TCQD and 1 mmole of phenothiazine was refluxed in 20 ml of dimethylformamide (DMF) for 1 h, after which it was poured into 300 ml of water, and the precipitate was removed by filtration and dried. The product was purified by column chromatography (SiO_2, ether) and subsequent recrystallization.

α,α'-Bis[3-(N-methylphenothiazinyl)]-p-phenylenedimalononitrile (Ic). This compound was obtained in the same way as Ib.

α-(3-Phenoxazinyl)-α'-[4-(N,N-dimethylaminophenyl)]-p-phenylenedimalononitrile (VIa). A) A mixture of 1 mmole of TCQD, 1 mmole of phenoxazine, 1 mmole of α-[4-(N,N-dimethylaminophenyl)]-p-phenylenedimalononitrile, and 50 ml of alcohol was refluxed for 10 h, and the resulting white precipitate was removed by filtration and dissolved in 15 ml of boiling acetonitrile. The hot solution was filtered to remove the undissolved compound (Ia, identified by TLC). Cooling of the mother liquor precipitated VIa, which was removed by filtration and recrystallized once more with activated charcoal.

B) A mixture of 1 mmole of chloranil, 1 mmole of phenoxazine, 1 mmole of V, and 30 ml of acetonitrile was refluxed for 5 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized twice from acetone to give the product in 40% yield.

C) A mixture of 1 mmole of benzoquinone, 1 mmole of phenoxazine, 1 mmole of V, and 30 ml of acetonitrile was refluxed for 5 h, after which the precipitate was recrystallized to give VIa in 37% yield.

α-(3-Phenothiazinyl)-α'-[4-(N,N-dimethylaminophenyl)]-p-phenylenedimalononitrile (VIb). This compound was obtained in the same way as VIa by methods A-C.

1,2-Bis[4-(α,α-dicyano-p-N,N-dimethylaminobenzyl)phenyl]-1,1,2,2-tetracyanoethane (VII). A mixture of 1 mmole of chloranil, 1 mmole of V, and 30 ml of acetonitrile was refluxed for 2 h, after which the precipitate was removed by filtration and recrystallized twice from acetonitrile with activated charcoal to give VII (27%) with mp 205°C (mp 203-204°C [5]).

Tetracyanoquinodimethane—3,7-dimethylphenothiazine Molecular Complex. Boiling solutions of equimolar amounts of TCQD and 3,7-dimethylphenothiazine in the minimum amount of acetonitrile were mixed, the mixture was cooled, and the precipitated black crystals were removed by filtration and dried to give a product with mp 225°C (dec.) in 98% yield. Found: C 72.3; H 3.9; N 16.3%. $C_{12}H_4N_4 \cdot C_{14}H_{13}NS$. Calculated: C 72.4; H 4.0; N 16.2%. The starting complex was isolated after it was refluxed for 10 h in acetonitrile or for 1 h in DMF.

LITERATURE CITED

1. B. P. Bespalov and E. V. Getmanova, Zh. Org. Khim., 16, 2358 (1980).
2. B. P. Bespalov, E. V. Getmanova, A. A. Pankratov, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 12, 1633 (1976).
3. A. L. Mndzhoyan (editor), Syntheses of Heterocyclic Compounds [in Russian], No. 5, Izd. Akad. Nauk Armyansk. SSR (1960), p. 56.
4. D. S. Acker and W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).
5. B. P. Bespalov, Zh. Org. Khim., 16, 839 (1980).

ACID—BASE PROPERTIES OF 1,2,5-OXADIAZOLES.

2.* AMINOFURAZANS

I. V. Tselinskii, S. F. Mel'nikova,
and S. N. Vergizov

UDC 547.793.2:543.422.6

The behavior of 3-R-4-aminofurazans (R = NH_2, CH_3, OCH_3, N_3, COOH, and NO_2) in sulfuric acid solutions was studied by electronic and PMR spectroscopy. The constants of protonation (pK_{aBH^+}) at the amino group and in the ring were calculated from the changes in the spectra. Dependences of the position of the absorption maxima corresponding to $\pi \rightarrow \pi^*$ transitions and the pK_{aBH^+} values and with the σ° substituent constants were found.

In order to predict the behavior of furazan derivatives in acid-catalyzed reactions by a spectrophotometric method we investigated the protonation of 3-substituted 4-aminofurazans and calculated the corresponding acidity constants.

The absorption maximum corresponding to a $\pi \rightarrow \pi^*$ transition in unsubstituted furazan lies in the "vacuum" UV region [2]. The introduction of an amino group, which is capable of conjugation with the ring, gives rise to a decrease in the energy of the transition (Table 1). A hypsochromic shift of the absorption band is observed as the electron-acceptor properties of the substituent in the 3 position increase; the position of the maximum correlates with the σ_m° substituent constants:

$$\nu \cdot 10^{-4}\ (\mathrm{cm}^{-1}) = (4{,}02 \pm 0{,}05) + (0{,}80 \pm 0{,}12)\,\sigma_m^0 \qquad (n=5,\ r=0{,}967,\ s=0{,}02). \tag{1}$$

Aminofurazancarboxylic acid deviates from the correlation; this is probably associated with the presence of an intramolecular hydrogen bond.

---

*See [1] for Communication 1.

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 321-324, March, 1981. Original article submitted March 4, 1980.

0009-3122/81/1703-0228$07.50

© 1981 Plenum Publishing Corporation